

Article

## Temporal Variability of Atmospheric Total Gaseous Mercury in Windsor, ON, Canada

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**Abstract:** Atmospheric Total Gaseous Mercury (TGM) concentrations were monitored in Windsor, Ontario, Canada, during 2007 to 2011, to investigate the temporal variability of TGM. Over five years, the average concentration was  $2.0 \pm 1.3$  ng/m<sup>3</sup>. A gradual decrease in annual TGM concentrations from 2.0 ng/m<sup>3</sup> in year 2007 to 1.7 ng/m<sup>3</sup> in 2009 was observed. The seasonal means show the highest TGM concentrations during the summer months ( $2.4 \pm 2.0$  ng/m<sup>3</sup>), followed by winter ( $1.9 \pm 1.4$  ng/m<sup>3</sup>), fall ( $1.8 \pm 0.81$  ng/m<sup>3</sup>), and spring ( $1.7 \pm 0.73$  ng/m<sup>3</sup>). Diurnal patterns in summer, fall, and winter were similar. A different diurnal pattern was observed in spring with an early depletion in the morning. The TGM concentrations were lower on weekends ( $1.8 \pm 0.77$  ng/m<sup>3</sup>) than on weekdays ( $2.0 \pm 1.5$  ng/m<sup>3</sup>), suggesting 10% of TGM in Windsor was attributable to emissions from industrial sectors in the region. Directional TGM concentrations also indicated southwesterly air masses were TGM enriched due to emissions from coal-fired power plants and industrial facilities. Correlation and principal component analysis identified that combustion of fossil fuel, ambient temperature, wind speed, synoptic systems, and O<sub>3</sub> concentrations influenced TGM concentrations significantly. Overall, inter-annual, seasonal, day-of-week, and diurnal variability was observed in Windsor. The temporal patterns were affected by anthropogenic and surface emissions, as well as atmospheric mixing and chemistry.

**Keywords:** atmospheric mercury; total gaseous mercury; temporal variability; principal component analysis; directional concentrations; pollutant rose; long-range transport

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## 1. Introduction

Mercury (Hg) has been extensively used since ancient times in medical, agricultural, industrial, and scientific purposes because of its unique chemical and physical properties. Major anthropogenic sources of mercury emissions include coal-fired power plants, manufacturing of metal and chemical products, and waste incineration. Total atmospheric mercury consists of 97%–99% elemental mercury ( $\text{Hg}^0$ ), with the remaining 1%–3% encompassing particulate mercury and reactive gaseous mercury (RGM) [1,2]. Gaseous elemental mercury is slow-reacting, highly volatile, and sparsely soluble in water, leading to long atmospheric residence times, approximately 0.5–2 years [2]. Extensive use of mercury over the last several centuries, its long residence time—thus, global distribution by large-scale atmospheric circulations, and reemission of historical depositions resulted in an increased concentration of atmospheric mercury and consequent depositions by a factor of three to five compared with preindustrial periods [3]. In the northern hemisphere, current background atmospheric mercury concentrations range between 1.5 and 1.7  $\text{ng}/\text{m}^3$  [2]. Atmospheric mercury concentrations at these levels are not likely to affect human health. However, deposition of atmospheric mercury to aquatic surfaces and consequent bioaccumulation of mercury compounds in aquatic food webs at high concentration are highly toxic. The rate of mercury accumulation in an aquatic system is believed to be proportional to atmospheric mercury concentration [4].

Study of atmospheric mercury leads to better understanding of the impact of emission, chemistry, and deposition on mercury cycles among air, water, and land. A number of studies have been performed on atmospheric mercury concentrations in different rural [5–13] and urban [5,11,13–20] sites. Results of these studies indicated elevated mercury concentration and deposition in urban areas compared to rural locations. Different temporal patterns, *i.e.*, seasonal and diurnal variability, were also observed at urban sites. Temporal variability in urban settings was site specific, whereas most of the rural areas had a general pattern of a spring high and a fall low. The difference in concentration and variability between urban and rural sites observed could be due to differences in local sources, surface characteristics, meteorological conditions and presence of other pollutants in urban and rural sites [16]. To advance our understanding in regards to mercury emission, transport, transformation, and deposition processes, further studies are required in urban areas to facilitate source identification through measurements of atmospheric mercury along with a variety of air pollutants.

Windsor (Ontario, Canada) is an industrial city along the Canada-USA border (Figure 1). It is located downwind of several industrial states, including Michigan, Ohio, and Indiana, thus, experiencing trans-boundary air pollution. The combined effects from local anthropogenic sources and trans-boundary pollution have resulted in occasional poor air quality in Windsor [21]. Windsor is also at the heart of the Great Lakes region. Therefore, ambient mercury levels have significant implications on fish contamination. The objective of this study is to investigate the effects of emission, transport,

chemistry, and deposition processes on temporal variability of Total Gaseous Mercury (TGM) concentrations in Windsor.

**Figure 1.** Map of sampling location (★) at the University of Windsor, Ontario, Canada. (● represents Windsor Downtown Air Quality Station. Base maps adapted from Google Maps).



## 2. Methodology

### 2.1. Sampling Site and Instrumentation

The sampling site was located on the University of Windsor campus ( $42^{\circ}18.27'N$ ,  $83^{\circ}3.98'W$ ) (Figure 1). The site is on the north side of Wyandotte St. West (27 m) and opposite to the entrance roadway to the Ambassador Bridge—connecting Windsor and Detroit, Michigan in the US. The site is also close to Huron Church Road (approximately 200 m west), which is the major roadway for entering/exiting the Ambassador Bridge. Heavy local and border-crossing traffic in the nearby area of

the sampling site is due to the Ambassador Bridge and University of Windsor traffic. A monitoring campaign of 13 sites in 2006 revealed a rather homogeneous spatial distribution of TGM except for high concentrations near the Ambassador Bridge [22]. Hence, there are no significant local or urban sources of pollution that may bias TGM measurements at this site.

A Tekran<sup>®</sup> 2537A mercury vapor analyzer (Tekran Inc., Toronto, ON, Canada) was used to measure TGM concentration in the ambient air at 5 min intervals. Ambient air was collected at a height of 5 m above ground level. Hourly averaged TGM concentrations were calculated for the study period of 2007–2011, because the meteorological parameters and other air pollutants were available at hourly intervals. Quality Assurance and Quality Control procedures can be found in [22].

## 2.2. Meteorological Data and Other Air Pollutants

Hourly meteorological parameters for the years 2007–2011 were collected from the Environment Canada website [23], including surface air temperature, relative humidity (RH), wind speed, wind direction, and atmospheric pressure. These parameters were measured at Windsor International Airport, located approximately 10 km northwest of the sampling site.

Hourly ambient concentrations of carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), nitrogen oxide (NO), nitrogen dioxide (NO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), ozone (O<sub>3</sub>), and fine particulate matter (PM<sub>2.5</sub>) were downloaded from the Ministry of Environment Ontario website [24]. These data were collected at Windsor Downtown Air Quality Station, which is 2 km east of the sampling site (Figure 1).

## 2.3. Data Analysis

For seasonal analysis, the four seasons are winter—December, January, and February, spring—March, April, and May, summer—June, July, and August, and fall—September, October, and November. Day-of-week variability was analyzed for weekdays, Saturdays and Sundays. Diurnal variability was determined for the study period and by season. The analysis of variance (ANOVA) was used to check the statistical difference in mean concentrations between hour-of-day, day-of-week, seasons, and years. Tukey's test was used for comparisons of multiple means for various temporal scales.

To study the inter-relationships, Pearson correlation coefficients were calculated among twelve parameters. The parameters are hourly TGM concentrations, meteorological conditions (temperature, relative humidity, wind speed, and atmospheric pressure) and other air pollutants (CO, SO<sub>2</sub>, NO, NO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, and PM<sub>2.5</sub>). Furthermore, Spearman rank correlation coefficients and Kendall rank correlation coefficients were calculated because those two methods are less sensitive to outliers. Principal component analysis (PCA) with varimax rotation was conducted to identify the factors influencing TGM concentrations using the same twelve parameters as in the correlation analysis.

Wind rose was generated with WRPLOT View (Lakes Environmental, Waterloo, ON, Canada), using hourly wind speed and direction data. Hourly TGM and wind directions were used to produce pollutant rose at 10 degree intervals and percentile values of 5, 25, 50, 75, and 95th for concentrations in each of the 36 directions, using Grapher (R7, Golden Software, CO, USA).

All statistical analysis were performed at a confidence interval of 95% ( $\alpha = 0.05$ ), using MINITAB (R14, Minitab Inc., State College, Pennsylvania, PA, USA). The exception is PCA for which MATLAB (R2013a, MathWorks, Natick, Massachusetts, USA) was used.

### 3. Results and Discussion

#### 3.1. Temporal Variability

##### 3.1.1. Inter-Annual Variability

During 2007–2011, the TGM concentrations were in the range of 0.3–57 ng/m<sup>3</sup>; the average concentration was 2.0 ng/m<sup>3</sup> with a standard deviation of 1.3 ng/m<sup>3</sup>. This concentration was higher than the reported background value of 1.5–1.7 ng/m<sup>3</sup> for Hg<sup>o</sup> in the Northern Hemisphere, which constitutes 97%–99% of TGM [2]. The observed TGM concentration was also higher than the average value of 1.58 ng/m<sup>3</sup> observed at all CAMNet rural sites during 1995–2005 [8] and at Egbert, rural Ontario during 2000–2009 [25], and 1.45 ng/m<sup>3</sup> observed at Fort McMurray, Alberta, Canada during 2010–2013 [20]. However, it was close to 2.2–2.5 ng/m<sup>3</sup> observed in other urban sites, e.g., Toronto, Detroit, Connecticut, Alabama, and Nova Scotia [5,11,13,15,16].

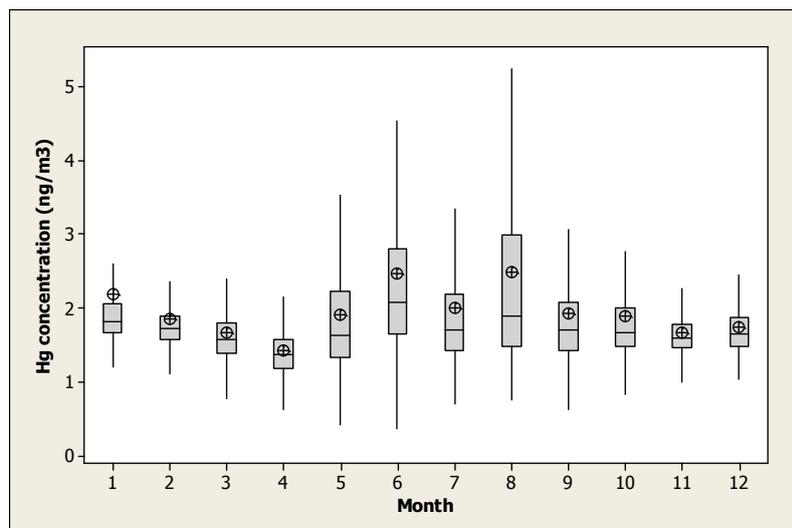
A gradual decrease in annual TGM concentrations from years 2007 to 2009 was observed (2007, 2.0 ± 1.8 ng/m<sup>3</sup>; 2008, 1.9 ± 0.99 ng/m<sup>3</sup>; 2009, 1.7 ± 1.15 ng/m<sup>3</sup>). TGM measurements in 2010 and 2011 were excluded from annual mean calculations due to uneven seasonal coverage, *i.e.*, data were missing for substantial parts of certain seasons. ANOVA and Tukey's tests indicate that the annual concentrations in 2007, 2008, and 2009 were statistically different.

The gradual decrease in TGM concentrations during 2007–2009 is consistent with decreasing trends observed at Egbert (a rural Ontario site, 400 km northeast of Windsor) and other mid-latitude or sub-arctic Canadian sites [25], and two background sites in New England [10] during the same time period. It is also consistent with the decreasing trends derived with land and cruise observations in both the Northern Hemisphere and Southern Hemisphere during 1996–2009 [26]. A 2007–2009 time series of TGM or elemental mercury in localities near Windsor and with industrial impact are not available in the literature yet. Nonetheless, the observed declines of mercury concentrations in precipitation at Mercury Deposition Network sites in the Northeast (−4.1 ± 0.49%/year) and Midwest (−2.7 ± 0.68%/year) US sites during 2004–2010 [27] are supportive of our finding. The gradual decrease in TGM concentrations is likely because of anthropogenic mercury emission reductions in the US [27] and Canada [28].

##### 3.1.2. Seasonal Variability

As shown in Figure 2, monthly TGM concentrations were high in the coldest (January) and warmest (May–August) months, and low in the transition months. A low *p*-value (<0.05) from ANOVA suggests statistically significant differences in the monthly means.

Seasonal patterns of TGM, SO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, wind speed, and ambient temperature are presented in Figure 3. The highest seasonal TGM concentration was observed in summer (2.4 ± 2.0 ng/m<sup>3</sup>), followed by winter (1.9 ± 1.4 ng/m<sup>3</sup>), while low in fall (1.8 ± 0.81 ng/m<sup>3</sup>) and spring (1.7 ± 0.73 ng/m<sup>3</sup>). Results of ANOVA and Tukey's test indicate the differences in all four means were statistically significant. A lower variation of TGM concentration was found during the spring and fall seasons, while higher variation was found in summer and winter.

**Figure 2.** Monthly TGM concentrations during 2007–2011 in Windsor.

As expected, ambient temperatures were highest in summer ( $22.6 \pm 4.5$  °C) and lowest in winter ( $-2.9 \pm 5.4$  °C). Wind speed was high in winter ( $17.6 \pm 9.6$  km/h) and spring ( $16.9 \pm 9.6$  km/h), and low in summer ( $12.0 \pm 7.6$  km/h). O<sub>3</sub> concentrations were high in spring ( $32.6 \pm 14$  ppb), peaked in summer ( $35.6 \pm 18$  ppb), but low in fall ( $20.7 \pm 14$  ppb) and winter ( $17.9 \pm 10$  ppb). An opposite seasonal trend was observed for NO<sub>x</sub> (Figure 3f) and CO (not shown). SO<sub>2</sub> concentrations were right skewed. While the medians were similar throughout the four seasons, the mean value was higher in winter ( $4.9 \pm 7.2$  ppb), indicating strong influences of air masses with enriched SO<sub>2</sub>, especially during the cold season.

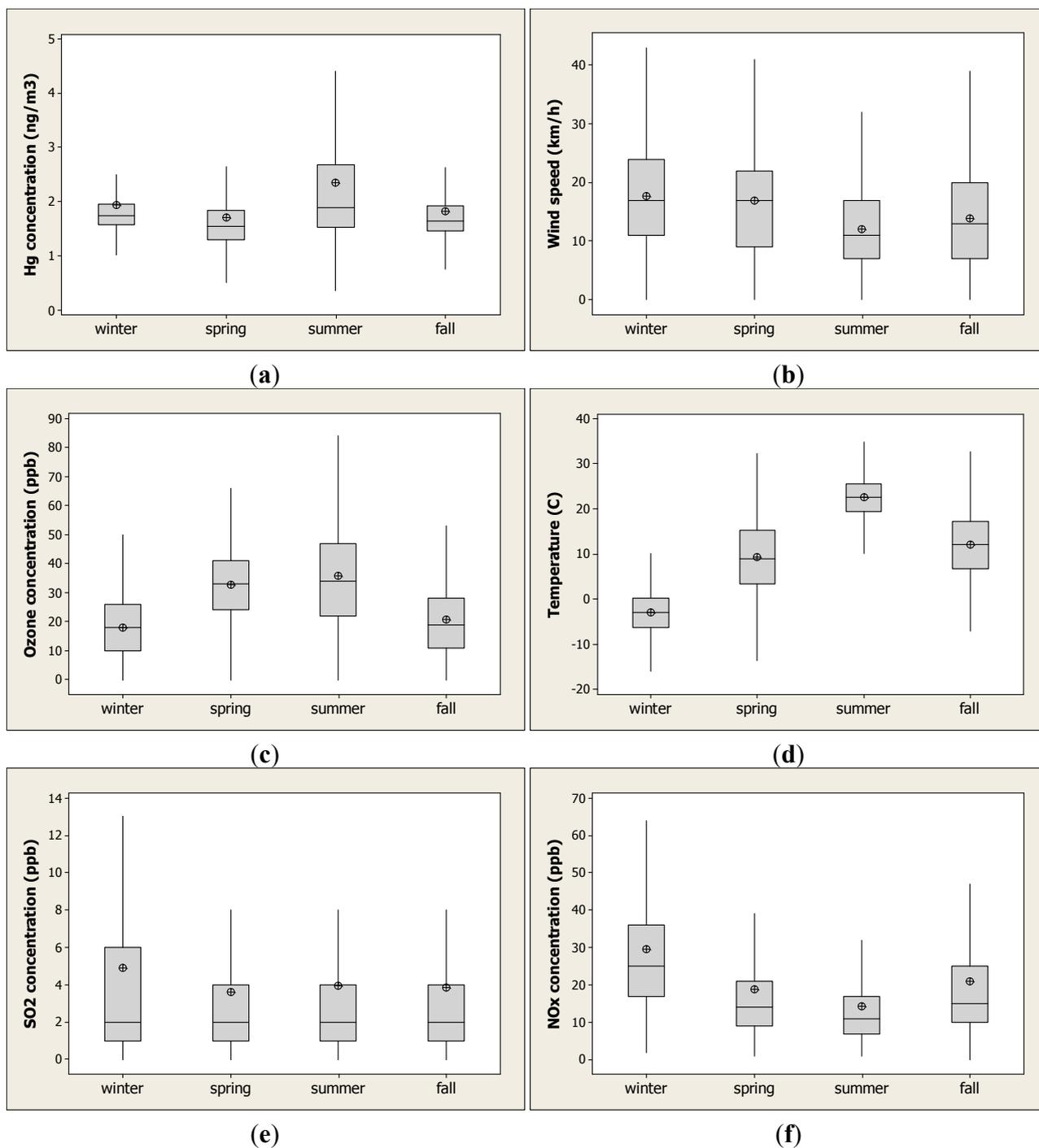
Overall, summer in Windsor is characterized by high temperature leading to high Hg reemission, more coal consumption, and lower wind speed thus less dispersion. On the other hand, higher concentrations of photo-chemical oxidants, such as O<sub>3</sub>, would result in transformation of Hg<sup>0</sup> and sequential deposition. The elevated TGM concentrations observed were the net effect of all above-mentioned processes.

The seasonal patterns of higher summer concentrations, in comparison with other seasons observed in this study, are quite similar to most of the studies conducted at urban sites in North America [5,15,16]. Winter TGM concentration in Windsor was relatively high—similar as observed in Toronto, Canada [15]. However, the pattern in Windsor was different from the spring high and fall low seasonal pattern observed in North American rural sites [5,8,11,29].

Difference in meteorological conditions, as well as atmospheric chemistry between urban and rural sites, could lead to elevated TGM concentrations in summer [16]. A study conducted in several urban sites in New York [14] suggested that the emissions from urban surfaces could elevate urban mercury concentration. For example, higher mercury fluxes during summer from soil, grass, and pavement were observed at an urban site [30]. Another possible reason for high concentrations in summer could be the increased electricity demand resulting in more coal combustion. During 2007–2011, the highest quarterly US national coal consumption in the electric power sector was recorded in July–September, ranging 26%–28% (average 27%) of the annual values [31]. Though there is no coal fired-power plant in Windsor, US states to the south and west of Windsor, e.g., Indiana, Illinois, Ohio, and Michigan, are the largest mercury point sources in North America [32]. Five coal-fired power plants located in

Ontario, Canada, also emit one third of the total mercury emissions in Ontario [33]. Thus, transportation of airborne mercury from regional sources could affect TGM concentrations. In addition to higher emissions, lower wind speeds during the summer cause less dilution of atmospheric mercury, resulting in a build-up of mercury concentrations.

**Figure 3.** Box plot of seasonal (a) TGM, (b) wind speed, (c) O<sub>3</sub>, (d) temperature, (e) SO<sub>2</sub>, (f) NO<sub>x</sub>, during 2007–2011 in Windsor.



A possible reason for higher concentrations in winter could be the increase in heating demand, resulting in more coal combustion [15]. Low atmospheric oxidant, e.g., O<sub>3</sub> concentrations, and low removal rate of atmospheric mercury in colder seasons, could also result in high concentrations [34].

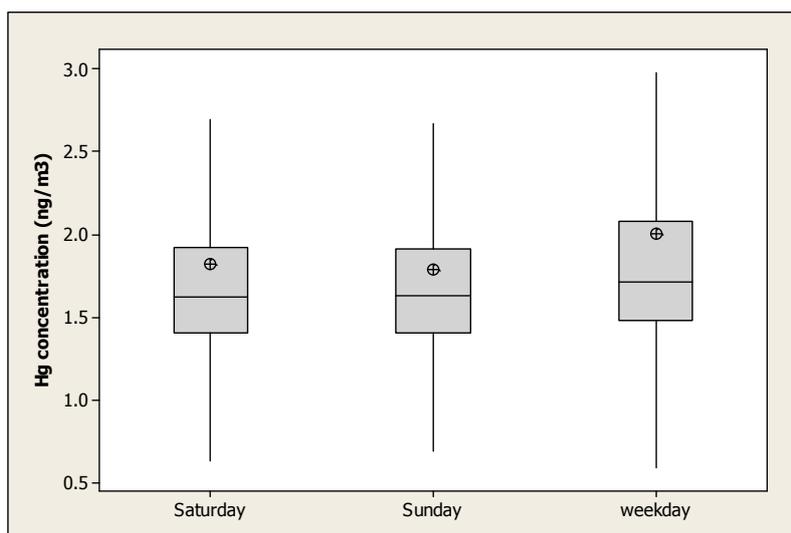
For fall and spring, lower ambient temperatures compared to the summer, and less coal consumption than in winter/summer may lead to lower concentrations.

### 3.1.3. Day-of-Week Variability

Weekdays had higher levels of TGM and higher variability ( $2.0 \pm 1.5 \text{ ng/m}^3$ ) when compared to Saturdays ( $1.8 \pm 0.71 \text{ ng/m}^3$ ) and Sundays ( $1.8 \pm 0.77 \text{ ng/m}^3$ ), shown in Figure 4, because of more emissions from anthropogenic sources, as pointed out by Brooks *et al.* [35]. The differences between Saturdays and Weekdays, as well as between Sundays and Weekdays, were statistically significant.

The difference between weekday and weekend means were  $0.2 \text{ ng/m}^3$ , implying at least 10% of observational TGM in Windsor was attributable to mercury emissions by the industrial sector in this study region. This estimate is consistent with simulation results of a global model [36]. They found North American emissions accounted for approximately  $0.3\text{--}0.4 \text{ ng/m}^3$  of the total mercury observed at the non-Arctic CAMNet sites.

**Figure 4.** Box plot of day-of-week TGM during 2007–2011 in Windsor.

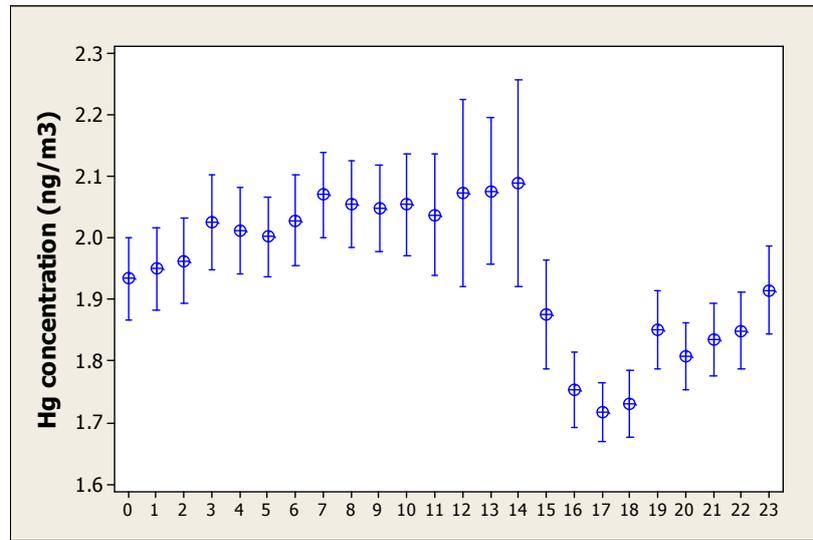


### 3.1.4. Diurnal Variability

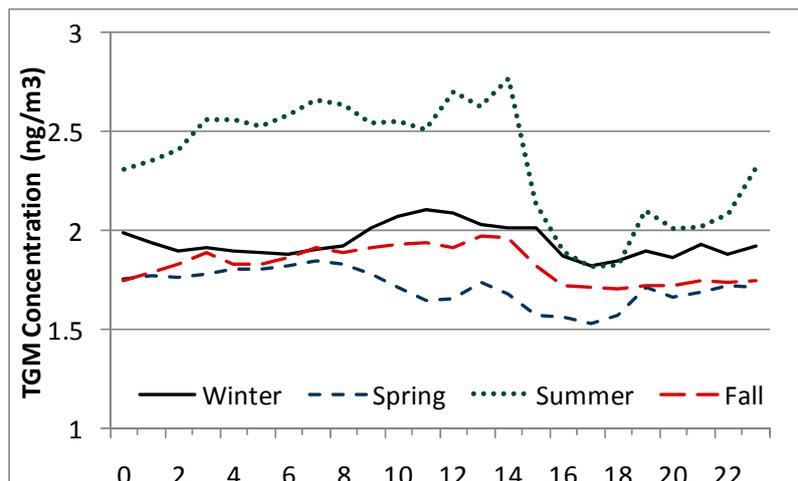
Figure 5a depicts the diurnal distribution of hourly TGM concentration during the study period. From hours 00:00 to 14:00, there was a gradual increase in TGM concentrations, followed by a comparatively steep decrease when ambient temperature and  $\text{O}_3$  concentrations peaked, *i.e.*, at 14:00. A small spike in concentration occurred at hour 19:00, which was followed by another slow and gradual concentration increase for the remainder of the day. Results of ANOVA indicate there were significant differences in means among the hours. However, all Tukey groups had overlapped due to large within-hour variances as opposed to between-hour variances.

After reviewing a number of studies reporting urban TGM diurnal cycles, it was found that each study had reported a site-specific diurnal trend [11,13,15,16,19,20,22,34]. In our study, decreasing concentration in the afternoon, followed by an increasing concentration at night was observed. This diurnal cycle is similar to that reported in Detroit [16]. The similarity in concentration trends is likely due to similar emissions and meteorological characteristics in these two neighboring cities.

**Figure 5.** Hour-of-day TGM (a) during 2007–2011 (circles are means and bars represent 95% confidence intervals of means), and (b) by season.

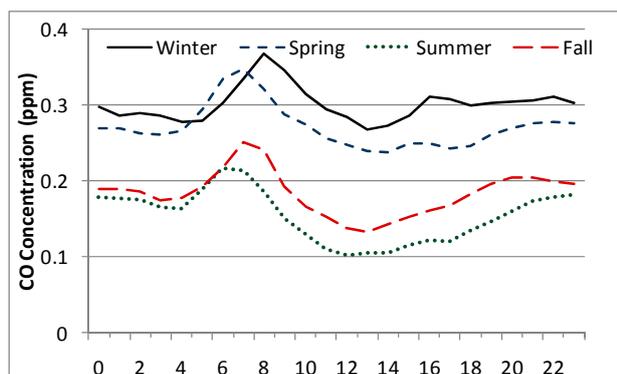


(a)

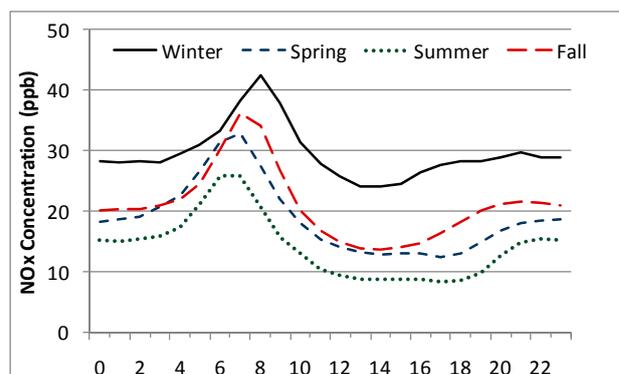


(b)

**Figure 6.** Seasonally averaged hour-of-day trends of meteorological conditions and air quality. (a) CO; (b) NO<sub>x</sub>; (c) O<sub>3</sub>; (d) Temperature; (e) SO<sub>2</sub>; (f) Wind speed; (g) PM<sub>2.5</sub>; (h) Relative humidity.

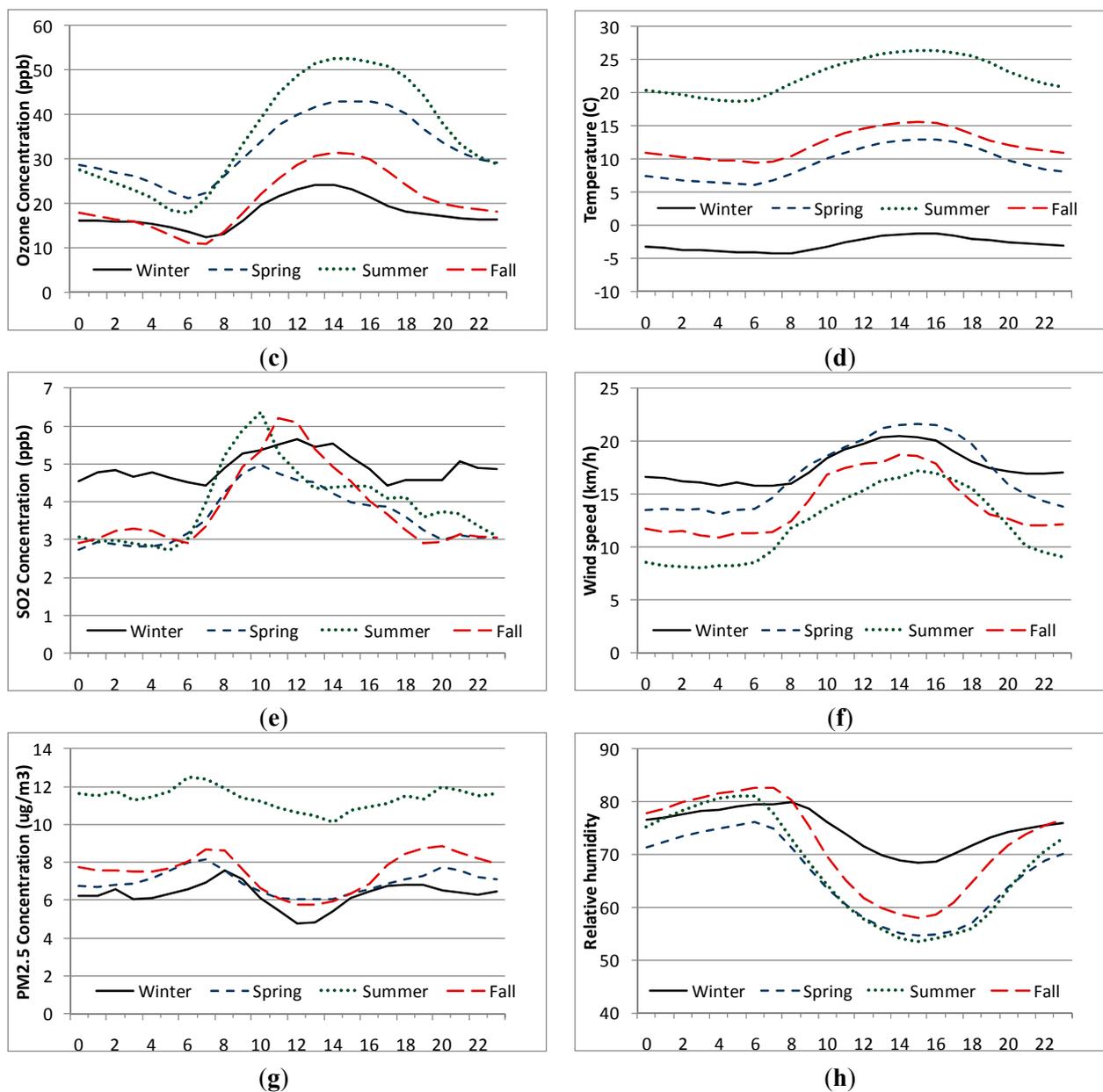


(a)



(b)

Figure 6. Cont.



As shown in Figure 5b, in summer, winter, and fall the TGM diurnal patterns were similar to the entire study period (Figure 5a). The increases before sunrise track that of CO and NO<sub>x</sub>, reflecting nocturnal inversions. After sunrise, TGM followed the diurnal temperature cycle (Figure 6). There was a depletion in the afternoon that continued until early evening. The diurnal pattern was significantly different in spring compared to other seasons; TGM depletion started in the morning instead of the afternoon.

In winter, summer, and fall, the TGM concentration followed the diurnal temperature trend from morning until noon. In this time period, the increase in TGM could be governed by solar radiation/temperature driven surface emissions and enhanced biological activities, *i.e.*, foliar emission especially in summer and fall [15,37]. Regardless of season, a decrease in afternoon concentration was observed when the O<sub>3</sub> concentrations were high (Figure 6c). This supports the mechanism of TGM depletion by oxidation. An increased level of photo-chemically originated oxidants (e.g., O<sub>3</sub>) in the afternoon could lead to oxidation of Hg<sup>0</sup> to RGM which is then rapidly deposited, resulting in

a decrease in overall TGM concentrations [34]. Several studies in urban sites [7,38] have reported high RGM concentrations between solar noon and late evening hours, causing an overall decrease in TGM concentrations similar to this study. In the afternoon there were also increased surface reemissions. However, the strong presence of increased vertical mixing and oxidation resulted in an overall downward trend. We hypothesize that the early depletion in spring morning is due to an increase in the atmospheric oxidation rate, following O<sub>3</sub> concentrations, and lower rates of reemissions, following ambient temperature and owing to reduced vegetative covers.

In summer, the rate of TGM increase from evening to morning and the rate of decrease in afternoon were higher compared to other seasons (Figure 5b). Formation of photo-chemical oxidants such as O<sub>3</sub> in the presence of high solar radiation and high temperature is greatest in the summer, which could lead to a steeper TGM decline in the afternoon during this season. Large variability in the summer could be due to greater diurnal variations in temperature and mixing height, a higher rate of uptake/emission by vegetation, increased surface emissions, and enhanced oxidation in warmer seasons [8,13,37,39]. In spite of afternoon concentration depletion, nighttime TGM levels were elevated when compared with other seasons. Higher anthropogenic emissions due to cooling demands and significant surface emissions may lead to the overall higher TGM concentration in summer, as observed in seasonal variability.

Overall, TGM temporal variability analysis indicates influence by environmental conditions, such as meteorological parameters, presence of oxidants, atmospheric chemistry, and local/regional sources. To understand the impact of these processes on temporal variability of TGM, relationships between TGM concentrations and meteorological parameters as well as other air pollutants are further investigated in the following two sections.

### 3.2. Environmental Factors Influencing TGM

To further investigate the relationships on an hourly basis, Pearson correlation coefficients for hourly TGM and other air contaminant measurements, and meteorological parameters are presented in Table 1. Cross-correlation matrixes of all 12 valuables can be found in Figure S1 (Supplemental Materials).

**Table 1.** Pearson correlation coefficients of hourly Total Gaseous Mercury (TGM) concentration with other parameters (all significant at  $p < 0.05$  except shaded cells).

Parameter	2007–2011 (N = 23,467)	Winter (N = 5303)	Spring (N = 6041)	Summer (N = 5512)	Fall (N = 6612)
SO <sub>2</sub>	−0.008	0.046	0.031	−0.045	−0.039
NO	0.083	0.084	0.188	0.112	0.162
NO <sub>2</sub>	0.106	0.117	0.288	0.130	0.146
NO <sub>x</sub>	0.105	0.109	0.269	0.142	0.177
CO	0.100	0.105	0.318	0.178	0.190
O <sub>3</sub>	−0.068	−0.090	−0.227	−0.106	−0.092
PM <sub>2.5</sub>	0.074	0.067	0.248	−0.021	0.053
Temperature	0.090	−0.084	0.144	−0.042	0.112
Relative humidity	0.078	−0.007	0.251	0.108	0.006
Wind speed	−0.083	0.025	−0.216	−0.051	−0.068
Pressure	−0.073	−0.022	−0.115	−0.076	−0.063

When the five-year dataset was considered, hourly TGM had weak but significant positive correlations with NO, NO<sub>2</sub>, NO<sub>x</sub>, CO, PM<sub>2.5</sub>, temperature, and relative humidity; weak negative correlations with O<sub>3</sub>, wind speed, and pressure. A New England study also found positive correlations with NO<sub>y</sub> and CO in winter [40]. The average SO<sub>2</sub> concentration over the study period was 4.1 ppb, with higher seasonal levels in winter (4.9 ppb) and summer (4.0 ppb). The much anticipated positive correlation with SO<sub>2</sub> due to coal combustion [41,42] was absent. In other words, mercury emissions from coal-fired power plants may not significantly increase TGM in regions a few hours downwind [39] due to the depositional removal of more soluble and reactive oxidized Hg from the plume as it is advected to the Windsor measurements site. Monitoring of speciated mercury is needed to further investigate the Hg-sulfur relation. Another possible reason is the TGM-SO<sub>2</sub> association was damped by the long-term record. Our result is similar to that of a short-term 2007 study in Windsor [22], and to the findings in New England [40] and in Seoul, Korea [19]. Among the four seasons, the relationships were similar but strongest in spring, while winter TGM was only correlated with one (temperature) out of four weather conditions.

Focusing on coefficients >0.2 in spring, the direction (*i.e.*, positive or negative) of the correlation is indicative. Positive correlations, although weak, of TGM with NO, NO<sub>2</sub>, NO<sub>x</sub>, CO, and PM<sub>2.5</sub>, suggest fossil fuel combustion as the common source. Negative correlation with wind speed indicates a decrease in concentration at high wind speeds because of dilution of air pollutants, including mercury. Anti-correlation with O<sub>3</sub> points toward oxidation of Hg<sup>0</sup>. TGM was positively correlated with RH. However, the correlation was negative when RH ≥ 99%, although not significant ( $r = -0.267$ ,  $p > 0.05$ ). High ambient RH leads to condensation of water vapor. Removal of gaseous mercury from the atmosphere is enhanced due to rapid oxidation of elemental mercury in the aqueous phase [1]. Thus, high water contents could lead to enhanced oxidation, resulting in deposition of atmospheric mercury.

Similar results were observed with the Spearman rank correlations (Table 2) and Kendall rank correlations (Table S1). In comparison with the Pearson correlations (Table 1), the differences among the four seasons were less pronounced when rank correlations were employed, especially between TGM and other pollutants. The results indicate that the relationships in spring were less affected by extreme concentration values. Nonetheless, the directions of the correlations were largely unaltered by rank correlations. Therefore, the conclusions regarding emission sources and weather conditions influenced temporal variability of TGM significantly remain the same.

Although most correlations listed in Tables 1 and 2 are statistically significant, they are of little practical significance because coefficient values were low. The contrast between moderate to strong correlations on the seasonally averaged diurnal trends and the weak correlations on the basis of hourly data is striking. Figure 6 shows strong correlations among seasonally averaged hour-of-day temperature, RH, wind speed, O<sub>3</sub>, PM<sub>2.5</sub>, and SO<sub>2</sub> concentrations. However, those associations were all lost on an hourly basis, except for the anti-correlation between temperature and RH in summer (Figure S1). On the other hand, the lack of strong association between hourly TGM and other parameters, particularly in winter [17], is not unexpected. One possible reason is the large variability of each parameter, which is governed by different atmospheric physical and chemical processes of different time and spatial scales. Therefore, the apparent associations in seasonally averaged trends were diminished by substantial scattering in the hourly data. Another explanation is the existence of a rather stable and homogeneous distribution of TGM over North America, especially in the winter [29]. Consequently, factors modulating TGM levels above and

beyond the diurnal cycles are difficult to identify. In-depth analysis of episodic events as in [29] may provide insightful relationships, which could be easily marginalized in long-term time series analysis.

**Table 2.** Spearman rank correlation coefficients of hourly TGM concentration with other parameters (all significant at  $p < 0.05$  except shaded cells).

Parameter	2007–2011 (N = 23,467)	Winter (N = 5303)	Spring (N = 6041)	Summer (N = 5512)	Fall (N = 6612)
SO <sub>2</sub>	0.018	0.110	0.089	−0.082	−0.015
NO	0.205	0.382	0.165	0.228	0.245
NO <sub>2</sub>	0.305	0.349	0.398	0.336	0.271
NO <sub>x</sub>	0.311	0.399	0.381	0.356	0.309
CO	0.249	0.378	0.378	0.439	0.341
O <sub>3</sub>	−0.263	−0.294	−0.384	−0.273	−0.224
PM <sub>2.5</sub>	0.180	0.252	0.247	0.029	0.091
Temperature	0.065	−0.135	0.044	−0.115	0.071
Relative humidity	0.212	0.017	0.348	0.257	0.120
Wind speed	−0.186	−0.076	−0.265	−0.183	−0.122
Pressure	−0.142	−0.050	−0.145	−0.172	−0.120

The results of PCA over the five-year study period and by season are shown in Table 3. When analyzed by year, similar results were obtained as with the full dataset, as shown in Table S2. For comparison, the four or five factors with largest eigenvalues ( $\geq 0.93$ ) were retained. These factors explained 71%–80% of the total variances. The interpretation of each factor was based on the loadings and outcomes of other PCA studies of atmospheric mercury [16,17,19,20,22,39,42]. For example, in Table 3a, Factor 1 had strong positive loadings for NO, NO<sub>x</sub>, CO, and a weak positive loading for TGM. All these compounds have a common source, the combustion of fossil fuel. The impact of each factor on TGM was evaluated by TGM loading in that factor.

For the study period of 2007–2011, the dominant factor is Fossil Fuel Combustion, followed by Diurnal Trend (large loading of temperature), Photochemistry (large loadings of O<sub>3</sub> and RH with opposite signs) and PM<sub>2.5</sub>, Synoptic Systems (large loading of pressure), and Industrial Sulfur. The low loadings of TGM ( $< 0.15$ ) in the Photochemistry factor indicate its relatively small impact on TGM. The concurrent strong loadings of NO, NO<sub>2</sub>, NO<sub>x</sub> in the same factor (Table 3) are because of strong correlations among the three compounds (Figure S1).

The seasonal variation of PCA results is interesting. The two common factors influencing TGM variability are Fossil Fuel Combustion and Diurnal Trend. The impact of combustion on TGM has also been identified in most PAC studies in urban settings [16,17,19,22,39,42], with the exception of Fort McMurray, Alberta [20]. In winter (Table 3b), the Transport factor (large loading of wind speed) seems to be very influential to TGM (loading = 0.65), likely due to higher wind speeds (Figure 3). Photochemistry was only significant in spring (Table 3c), which is in agreement with a comparatively stronger correlation between TGM and O<sub>3</sub> than in other seasons (Table 1). In summer (Table 3d), Synoptic Systems (loading of pressure = 0.70) was a lead factor for TGM (loading = −0.49). The opposite signs suggest stagnant air during high-pressure systems not leading to TGM build-up, while high winds during low-pressure systems causing transport of TGM. In addition, summer is when TGM was only associated with two factors (TGM

loading > 0.15), verses three or four in other seasons, making it more challenging to pin-point the major mechanisms driving TGM variability in the warm months. The opposite loadings of SO<sub>2</sub> and TGM in spring, fall and winter under Industrial Sulfur contradict a 2007 short-term PCA study in Windsor, where a factor of Coal-fired Power Generation with positive loadings of SO<sub>2</sub> and TGM was identified [22]. A lack of strong association between TGM and Industrial Sulfur was also reported in Toronto, Ontario [17], Rochester, New York [39], and Fort McMurray, Alberta [20].

Overall, our correlation and PCA analyses suggest that the temporal variability of TGM was affected by man-made and surface emissions, atmospheric mixing and reactions, and aqueous chemistry. Future studies should conduct onsite measurement of mercury species, solar radiation, mercury fluxes, and potential oxidant/reductant concentrations to further examine the impact of environmental factors.

**Table 3.** Principal component analysis (PCA) factor loadings (bold numbers indicate loadings > 0.4). (a) 2007–2011; (b) Winter; (c) Spring; (d) Summer; (e) Fall.

(a)					
Parameter	Fossil Fuel Combustion	Diurnal Trend&PM <sub>2.5</sub>	Photo-Chemistry	Synoptic Systems	Industrial Sulfur
TGM	0.26	0.20	0.11	0.21	<b>0.67</b>
SO <sub>2</sub>	0.17	0.21	0.11	0.18	<b>-0.63</b>
NO	<b>0.48</b>	-0.06	0.11	-0.05	0.12
NO <sub>2</sub>	0.39	0.05	-0.16	-0.08	-0.13
NO <sub>x</sub>	<b>0.50</b>	-0.01	-0.01	-0.07	0.01
CO	<b>0.43</b>	-0.01	-0.02	0.17	-0.02
O <sub>3</sub>	-0.15	0.24	<b>0.48</b>	0.06	0.00
PM <sub>2.5</sub>	0.14	<b>0.62</b>	-0.05	0.00	-0.24
Temperature	-0.17	<b>0.56</b>	0.14	0.00	0.17
Relative humidity	-0.09	0.08	<b>-0.75</b>	0.11	0.00
Wind speed	0.01	-0.35	0.28	<b>0.59</b>	-0.16
Pressure	0.07	-0.15	0.22	<b>-0.72</b>	-0.09
Variance (%)	34.8	14.1	11.2	10.5	7.8
Eigen value	4.18	1.70	1.35	1.26	0.93

(b)				
Parameter	Fossil Fuel Combustion	Diurnal Trend	Transport	Industrial Sulfur
TGM	0.28	-0.10	<b>0.65</b>	-0.27
SO <sub>2</sub>	0.06	-0.05	0.06	<b>0.87</b>
NO	0.40	-0.04	0.06	-0.07
NO <sub>2</sub>	0.40	-0.06	-0.09	0.09
NO <sub>x</sub>	<b>0.45</b>	-0.06	0.00	-0.01
CO	0.39	0.04	0.07	-0.03
O <sub>3</sub>	-0.31	-0.22	0.15	-0.14
PM <sub>2.5</sub>	0.30	0.12	-0.09	0.19
Temperature	-0.12	<b>0.56</b>	-0.02	0.08
Relative humidity	0.10	<b>0.60</b>	-0.10	-0.13
Wind speed	-0.18	-0.06	<b>0.57</b>	0.27
Pressure	0.05	<b>-0.49</b>	<b>-0.44</b>	-0.03
Variance (%)	38.9	15.9	9.9	8.0
Eigen value	4.67	1.90	1.19	0.96

(c)

Parameter	Fossil Fuel Combustion	Diurnal Trend & PM <sub>2.5</sub>	Synoptic Systems & Photo-Chemistry	Transport & Industrial Sulfur
TGM	0.02	0.33	-0.30	-0.37
SO <sub>2</sub>	0.31	0.18	0.20	<b>0.49</b>
NO	<b>0.41</b>	-0.08	0.04	0.06
NO <sub>2</sub>	<b>0.43</b>	0.02	0.00	-0.07
NO <sub>x</sub>	<b>0.47</b>	-0.03	0.02	-0.01
CO	0.38	0.14	-0.14	0.04
O <sub>3</sub>	-0.27	0.29	0.28	0.16
PM <sub>2.5</sub>	0.24	<b>0.51</b>	0.01	-0.01
Temperature	-0.16	<b>0.65</b>	0.04	-0.04
Relative humidity	0.05	-0.14	<b>-0.60</b>	-0.10
Wind speed	-0.10	-0.10	-0.15	<b>0.68</b>
Pressure	0.11	-0.20	<b>0.62</b>	-0.34
Variance (%)	38.1	14.7	12.5	8.8
Eigen value	4.58	1.76	1.50	1.05

(d)

Parameter	Fossil Fuel Combustion	PM <sub>2.5</sub> & Industrial Sulfur	Synoptic Systems	Photo-Chemistry & Diurnal Trend
TGM	0.19	-0.12	<b>-0.49</b>	-0.05
SO <sub>2</sub>	0.08	<b>0.45</b>	0.13	-0.09
NO	<b>0.59</b>	-0.15	0.02	-0.15
NO <sub>2</sub>	0.36	0.21	-0.06	0.18
NO <sub>x</sub>	<b>0.54</b>	0.05	-0.03	0.04
CO	0.24	0.25	-0.36	0.07
O <sub>3</sub>	-0.19	0.27	0.02	-0.39
PM <sub>2.5</sub>	-0.04	<b>0.67</b>	-0.04	0.06
Temperature	-0.05	0.27	-0.14	<b>-0.48</b>
Relative humidity	-0.20	0.10	-0.25	<b>0.59</b>
Wind speed	-0.03	-0.19	-0.18	<b>-0.45</b>
Pressure	0.20	0.06	<b>0.70</b>	0.05
Variance (%)	34.4	17.4	10.9	9.0
Eigen value	4.12	2.09	1.31	1.08

(e)

Parameter	Fossil Fuel Combustion	Diurnal Trend & PM <sub>2.5</sub>	Synoptic Systems	Relative Humidity	Industrial Sulfur
TGM	0.24	0.15	-0.16	-0.16	<b>0.70</b>
SO <sub>2</sub>	0.20	0.14	-0.20	-0.25	<b>-0.61</b>
NO	<b>0.46</b>	-0.08	0.06	-0.14	0.12
NO <sub>2</sub>	<b>0.42</b>	0.02	0.06	0.10	-0.17
NO <sub>x</sub>	<b>0.51</b>	-0.05	0.07	-0.06	0.01
CO	0.40	0.06	-0.17	0.12	0.05
O <sub>3</sub>	-0.21	<b>0.41</b>	0.04	-0.31	0.01
PM <sub>2.5</sub>	0.18	<b>0.58</b>	0.02	0.22	-0.23
Temperature	-0.09	<b>0.63</b>	0.00	-0.06	0.14

Table 3e. Cont.

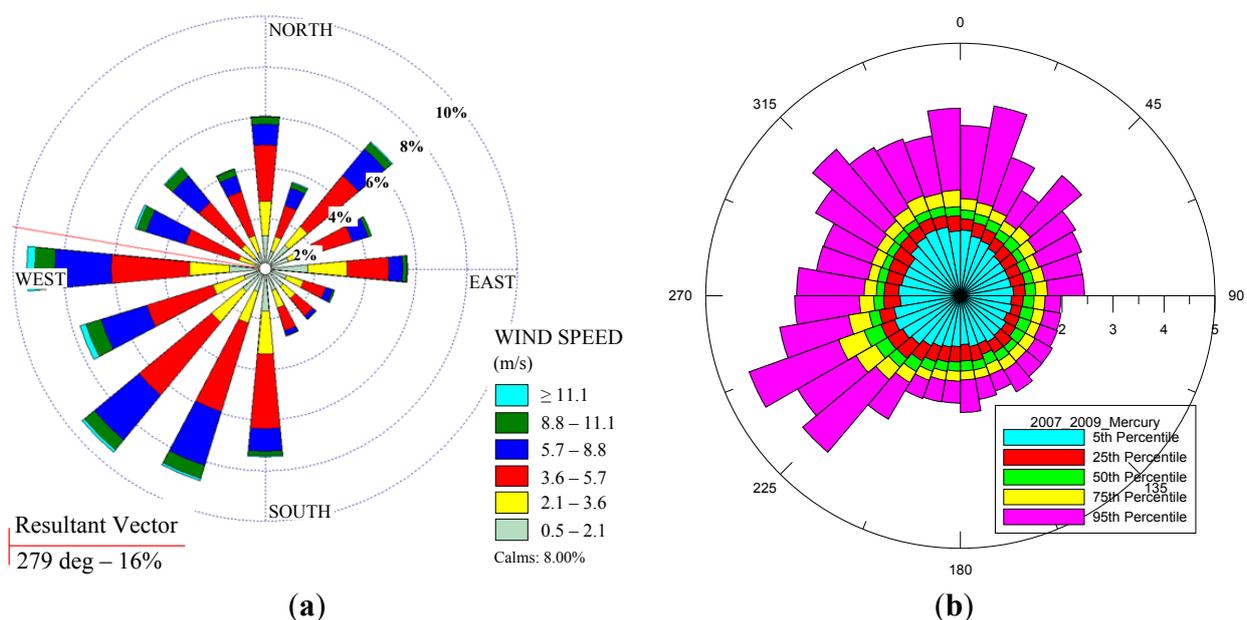
Parameter	Fossil Fuel Combustion	Diurnal Trend&PM <sub>2.5</sub>	Synoptic Systems	Relative Humidity	Industrial Sulfur
Relative humidity	-0.05	-0.01	-0.03	<b>0.75</b>	0.01
Wind speed	-0.08	-0.19	<b>-0.60</b>	-0.28	-0.09
Pressure	0.02	-0.10	<b>0.73</b>	-0.26	-0.07
Variance (%)	33.3	15.6	11.1	9.8	8.9
Eigen value	4.00	1.87	1.33	1.17	1.07

3.3. Directional TGM Concentrations

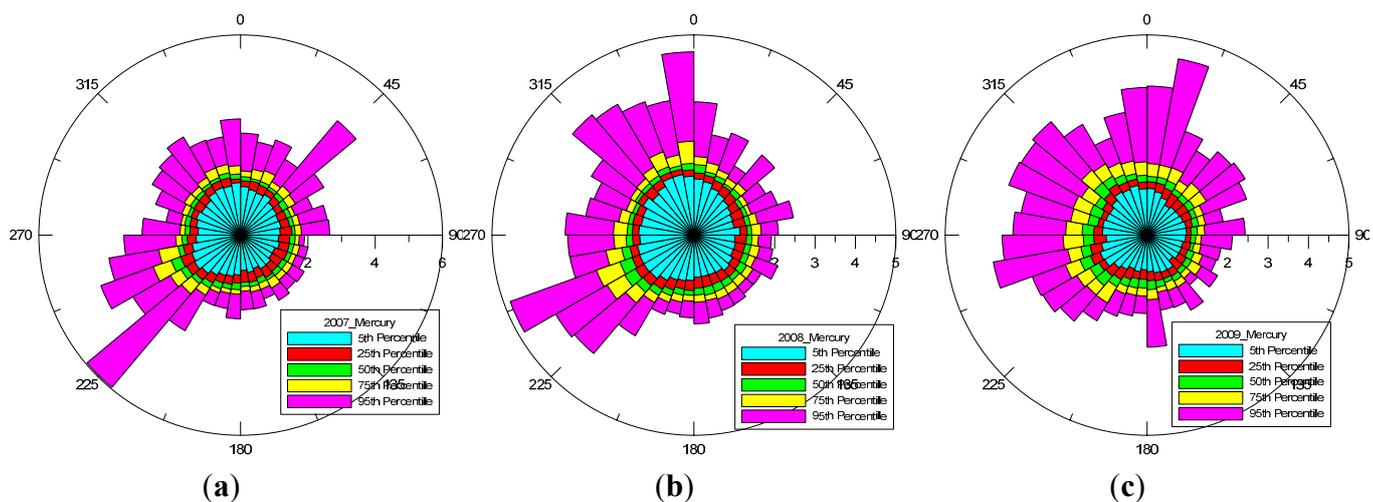
During this study, the prevailing winds were from the south to west (180–270°) section (Figure 7a), consistent with the long-term weather record in Windsor. Annual TGM roses in 2010 and 2011 were not generated due to uneven seasonal coverage in those two years. The TGM roses over 2007–2009 are shown in Figure 7b; a longer bar indicates a higher inter-percentile concentration. Higher TGM concentrations were associated with winds from the southwest (220–260°), while air masses from the east to south (90–200°) contained lower mercury concentrations. Similar patterns were observed on an annual basis in 2007 and 2008 (Figure 8). In 2009, the distribution of directional TGM concentrations was rather uniform, with the exception of extreme values, *i.e.*, 98th percentiles, by westerly and northerly winds (250° clockwise to 20°). Higher TGM associated with southwesterly air flow is due to coal-fired power generation and other industrial facilities located in the southwest region of Windsor. These sources have been identified through a back-trajectory and potential source contribution function investigation using the annual and seasonal TGM in 2007 [18].

The directional TGM distributions were similar in winter and spring, when air mass from the southwest brought in higher concentrations. In summer and fall, regions north of Windsor also contributed to elevated TGM levels (Figure 9). Further analysis is recommended to identify air mass conditions associated with those episodes.

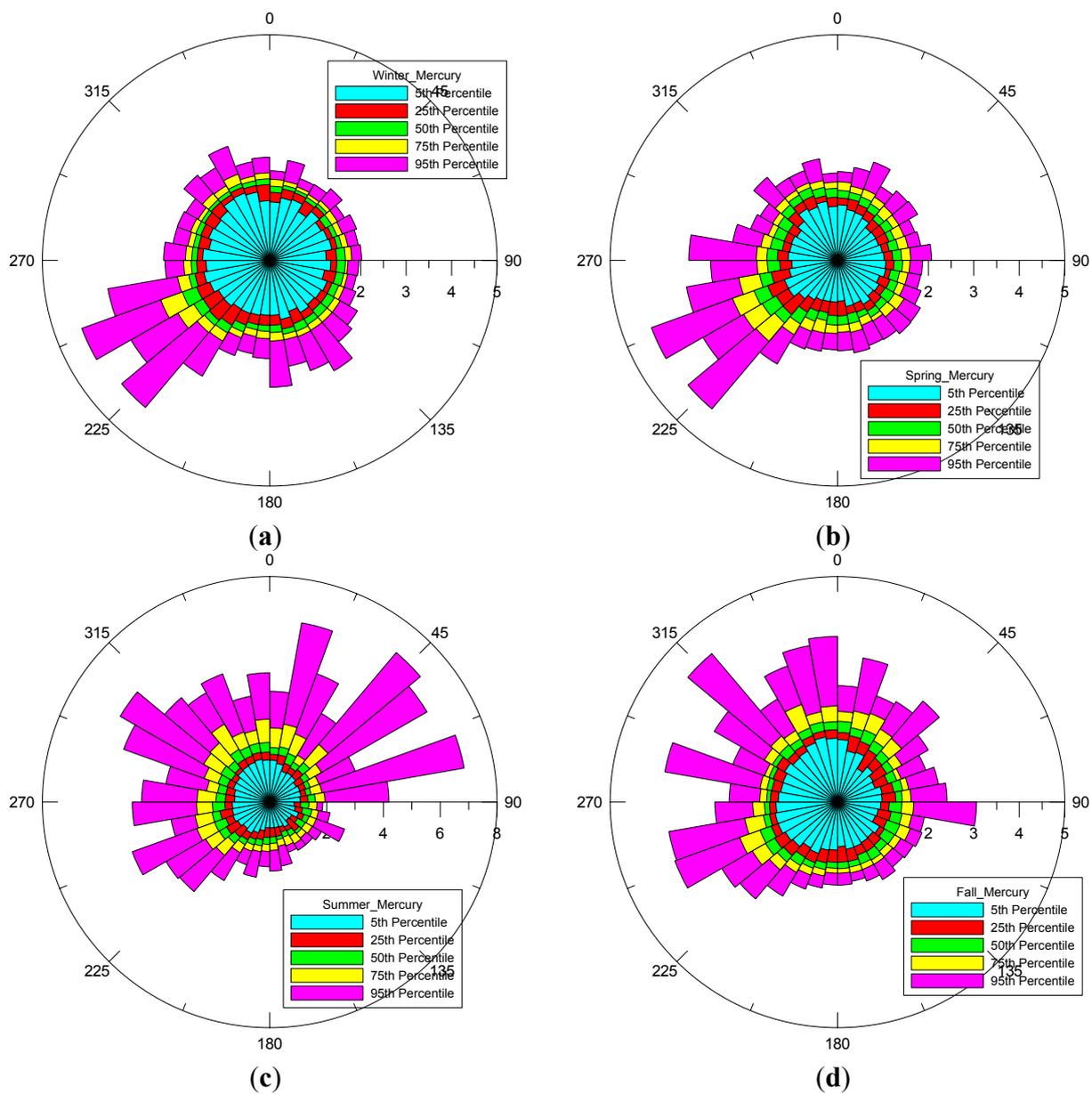
Figure 7. (a) Wind rose and (b) TGM concentration rose (ng/m<sup>3</sup>) during 2007–2009 in Windsor.



**Figure 8.** TGM concentration rose in (a) 2007, (b) 2008, and (c) 2009.



**Figure 9.** TGM concentration rose in (a) winter, (b) spring, (c) summer and (d) fall.



#### 4. Conclusions

This study monitored TGM concentrations from 2007 to 2011 in Windsor, which is an industrialized border city affected by local emissions and regional transport of air pollutants. The average concentration was  $2.0 \pm 1.3 \text{ ng/m}^3$ , which is higher than the concentration observed in all CAMNet sites in Canada (1995–2005), but close to the concentrations observed in other urban sites in North America. Different temporal aspects of TGM concentration were investigated. A gradual decrease in annual TGM concentrations from year 2007–2009 was observed ( $2.0\text{--}1.7 \text{ ng/m}^3$ ). TGM exhibited seasonality with the highest concentrations in summer, relatively high in winter, and low in spring and fall. High surface emissions in summer and an elevated anthropogenic mercury release from regional sources in summer and winter due to increased power consumption, most likely resulted in the elevated TGM concentrations in these two seasons. Weekday levels were higher than weekend levels by 10%, attributable to industrial activities in the region. On an annual basis, a distinctive diurnal pattern was observed. TGM concentration was relatively high overnight, followed by a continuous increase in the morning, a decline in the afternoon, minima in the early evening, and finally rising again. Diurnal patterns in winter, summer, and fall were similar to the annual pattern. However, spring diurnal trends were characterized by an early depletion due to the strong effect of oxidation loss, in conjunction with very little gain from vegetative reemission.

Environmental conditions, including temperature, relative humidity, wind speed, and  $\text{O}_3$  concentrations influenced temporal variability of TGM significantly. The associations between TGM and the study parameters were moderate to strong on seasonally averaged hour-of-day trends. The aforementioned relationships effectively explained the TGM diurnal cycles due to anthropogenic emissions, solar radiation/temperature driven surface emissions and mixing during the daytime, photochemical reactions in the afternoon, and atmospheric inversions at night. However, the analysis of hourly TGM and meteorological parameters, as well as  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_x$ ,  $\text{CO}$ ,  $\text{O}_3$ , and  $\text{PM}_{2.5}$  concentrations, did not yield any strong correlations. Our findings draw attention to the limitations imposed on the investigative power of correlation analysis using long-term hourly measurements.

The PCA results indicate combustion of fossil fuel as the major source of TGM. Directional analysis shows the southwesterly air masses were associated with higher TGM levels due to emissions from coal-fired power plants and industrial facilities. Diurnal cycles driven primarily by solar radiation (thus, temperature) and regional transport of air containments also significantly contributed to temporal variability of TGM. The impact of photochemistry, *i.e.*, reduction of ambient  $\text{Hg}^0$  by photochemical oxidation to RGM, was more clear to attribute in the spring because there are less confounding factors, *e.g.*, reemission of  $\text{Hg}^0$ .

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## Author Contributions

Xiaohong Xu, project PI, did literature review of some papers, analysis of variance (ANOVA), and wrote the manuscript. Umme Akhtar conducted data collection in 2007 and a few months in 2008, did literature review of some papers, and drafted some passages. Kyle Clark conducted compilation and screening of all data collected in 2007–2011, did general statistics, plotted most charts, and performed English correction of the manuscript. Xiaobin Wang conducted Principal Component Analysis (PCA), and did literature review of some papers.

## Conflicts of Interest

The authors declare no conflict of interest.

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